

UK Patent Application GB 2 241 963

(43) Date of A publication 18.09.1991

(21) Application No 9105316.5

(22) Date of filing 13.03.1991

(30) Priority data

(31) 07492695
07583051

(32) 13.03.1990
14.09.1990

(33) US

(51) INT CL⁶

C23C 22/07, C10M 107/34 137/02, C23C 22/56

(52) UK CL (Edition K)

C7U U4D U4E1 U4E2B U4E3 U4E4 U4F1 U4G1
U4H3 U4H4 U4J U4L U4M1 U4M2 U4R U7A
C5F FKG F103 F129

(71) Applicant

Henkel Corporation

(Incorporated in the USA - Delaware)

300 Brookside Avenue, Ambler, Pennsylvania 19002,
United States of America

(72) Inventor

Sami B Awad

(74) Agent and/or Address for Service

Sanderson and Co
34 East Stockwell Street, Colchester, Essex, CO1 1ST,
United Kingdom

(56) Documents cited

EP 0137057 A1 US 4859351 A US 4260469 A

(58) Field of search

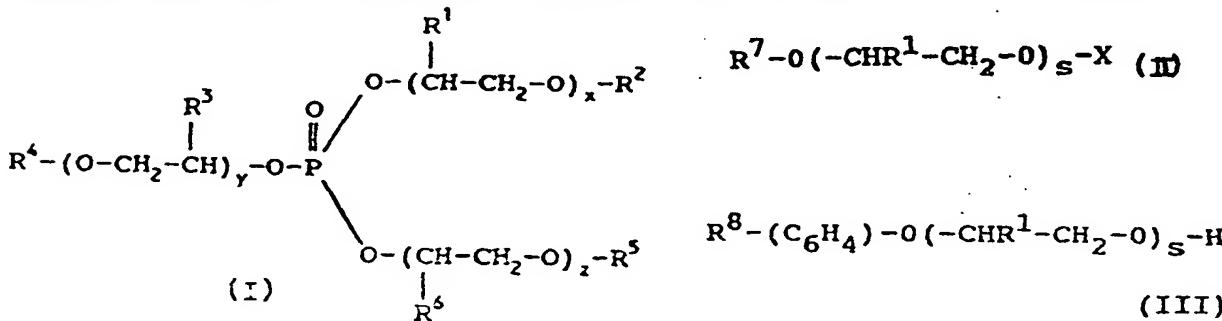
UK CL (Edition K) C5F FMA FMB, C7E, C7U
INT CL⁶ C10M, C23C, C23G

(54) Conditioning the surface of formed metal articles

(57) Articles such as aluminium cans, after forming and cleaning, are surface-conditioned to enhance their mobility in subsequent automatic handling operations by treatment while still wet from pre-cleaning with a multi-component aqueous composition containing certain water-soluble ethoxylated phosphate derivatives of general formula (I), water soluble Fe, Zr, Sn, Al or Co salts, water-soluble metal-etchants and other ethoxylated organic derivatives of general formulae (II) and (III). Preferably the compositions also include further components, namely chelating agents for the metal salts and/or still further ethoxylated organic derivatives of general formula (IV). The compositions may be operated at relatively acidic pH values where they are spared microbiological degradation, but preferably will nevertheless include an effective amount of biocide and/or anti-foaming agent. The results achieved are better than in the state of the art - in particular the compositions may be made up with tap water rather than deionized water, the treatment tends to remove spotting resulting from unplanned production stoppages, and the treated surfaces are notably free from "water-breaks".

In formula (I) each of R¹ R³ and R⁶, which may be the same or different, is hydrogen or an alkyl group (C₁₋₄), each of x, y, z is zero or an integer from 1 to 25 and each of R², R⁴ and R⁵, which may be the same or different, is hydrogen or a monovalent cation or a monovalent fraction of a polyvalent cation or an alkyl, aryl, or arylalkyl group (C₁₋₂₀), provided that at least one of R², R⁴, R⁵ (i) is not hydrogen and (ii) has at least one alkoxy group interposed between it and the phosphorus atom. In formula (II) R⁷ is a linear, cyclic or branched monovalent aliphatic hydrocarbon moiety (C₁₋₂₅), X is hydrogen, halogen, phenyl or R¹, and S = 150; and in formula (III) R⁸ is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety (C₄₋₂₅), and (C₆H₄) is an ortho-, meta-, para-phenylene nucleus.

In a second aspect metal surfaces are treated with a surface - conditioning composition based on water-soluble ethoxylated organic materials incorporating also a biocide, eg hydrogen peroxide, and/or an anti-foaming agent.



CONDITIONING THE SURFACE
OF FORMED METAL ARTICLES

This invention relates to the conditioning of the surface of formed metal articles.

It is more particularly directed to processes that produce on such formed metal articles, e.g. aluminium cans, a conditioned surface that is substantially or entirely free from "water breaks" when wet, or in other words a surface over which any water present on the surface spreads spontaneously; and also with compositions for use in those processes. More specifically this invention is concerned particularly with certain aqueous compositions, suitable for contacting formed metal surfaces to deposit thereon (after drying) a mobility-enhancing lubricant film, said compositions being protected against deterioration from the action of micro-organisms during storage and/or against foaming during use.

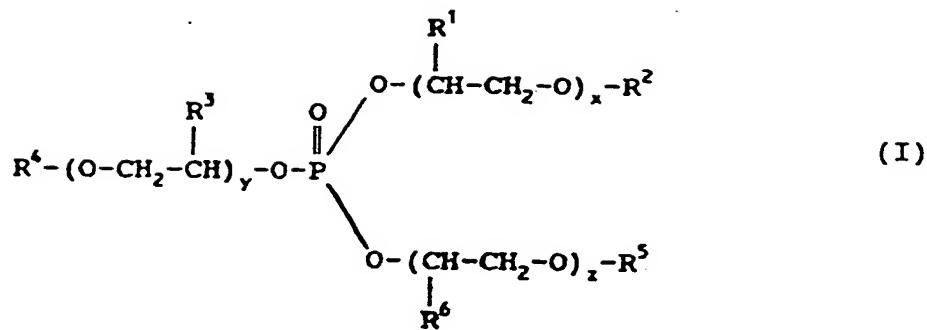
This invention stems from our continuing efforts to combat the problems that beset the high-speed production of aluminium beverage cans, as described in our United States Patent No. 4,859,351, and in that sense it is a development of and has some analogy with the procedures there described, though it should be emphasised that the present invention also in many ways is a clear departure

from those known procedures, and capable of achieving distinctly better results.

We have now found that a formed metallic and especially aluminium surface, which has in a conventional manner been thoroughly cleaned and de-greased by sufficient contact with a water-based acid or alkaline cleanser, can be effectively and advantageously surface-conditioned so as to impart increased mobility, i.e. a low coefficient of static surface friction, to the surface when subsequently dried, without harming the reflectivity or printability of the thus-treated surface or the adherence of lacquer thereto, by employment of processes involving treatment of the surface with certain compositions - which comprise or preferably consist essentially of water and the other components identified below.

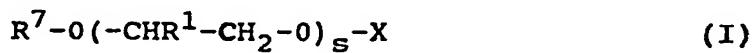
According to one aspect there is provided a process in which the surface of a previously-formed aluminium article, already de-greased and cleaned to remove aluminium fines and other solid contamination therefrom and thereafter water-rinsed, is treated by contact while still wet from the water-rinse with a liquid, aqueous multi-component composition which besides water comprises:

-(A) one or more water-soluble materials conforming to the general formula:



(wherein each of R^1 , R^3 and R^6 , which may be the same or different, is hydrogen or an alkyl group containing from 1 to 4 carbon atoms, each of x , y and z is zero or an integer from 1 to 25, and each of R^2 , R^4 and R^5 , which may be the same or different, is hydrogen or a monovalent cation or a monovalent fraction of a polyvalent cation or an alkyl, aryl or arylalkyl group containing from 1 to 20 carbon atoms, provided however that at least one of R^2 , R^4 and R^5 (i) is not hydrogen and (ii) has at least one alkoxy group interposed between it and the phosphorus atom;

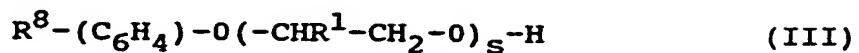
- (B) one or more water-soluble salts containing ions that include one or more Fe, Zr, Sn, Al and/or Ce atom(s);
- (C) one or more water-soluble metal-etching compounds;
- (D) one or more compounds conforming to the general formula:



(wherein R^7 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 1 to 25 carbon atoms, X is hydrogen, halogen, phenyl or R^1 , while s is an integer from 1 to 50, and R^1 has the same meaning as

in general formula I); and

-(E) one or more compounds conforming to the general formula:



(wherein R^8 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 4 to 25 carbon atoms, (C_6H_4) is an ortho, meta, or para phenylene nucleus, and R^1 and S have the same meanings as in general formula II above),

the amounts of components (D) and (E) being sufficient to stabilise the liquid composition against phase-separation.

It should be noted that not all of the specified components must be separate materials. Fluorozirconic acid (i.e. H_2ZrF_6) can for example serve simultaneously both as component (B) and as component (C).

It is preferable for component (A) to be a compound conforming to general formula I wherein each of x and z is zero, and each of R^2 and R^5 is hydrogen or a cation or cation fraction, and such materials can serve as all of components (A), (B) and (C), for example if R^2 is hydrogen and R^5 is $(1/3)Fe^{+3}$.

The metal-etching component (C) is preferably one or a mixture of more than one of the following acidic substances, namely nitric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, hydrochloric acid, hydrobromic acid and

hydroiodic acid, as well as acid salts of sulfuric and phosphoric acid, and also salts of nitric, sulfuric, phosphoric, hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids having an ionization product constant less than that of the acid with which they form the salt.

Preferably component (D) will be one or more of the compounds of general formula (II) wherein R⁷ contains from 4 to 20 carbon atoms, and/or s is an integer of from 1 to 20.

It is also preferred that component (E) should be one or more compounds of general formula (III) wherein R⁸ contains from 8 to 12 carbon atoms, and most advantageously 9 carbon atoms.

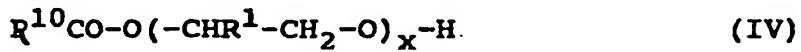
Optionally but preferably the multi-component composition also comprises:

-(F) one or more chelating agents for the metal-containing ions of component (B).

The chelating agents employed can advantageously be compounds (including polymers) the molecular structure of which contains at least two amino, substituted amino, carboxyl, phosphonate, sulfonate and/or carbonyl moieties.

Optionally but preferably the multi-component composition also comprises:

-(G) one or more compounds conforming to the general formula:



(wherein R^{10} is a linear or branched, saturated or unsaturated monovalent aliphatic hydrocarbon moiety containing from 1 to 25 carbon atoms; and R^1 and x have the same meaning as in general formula I).

The compound of general formula (IV) will desirably be one containing from 4 to 20 carbon atoms.

The process of this invention will normally include the preliminary preparation of a degreased, cleaned and still-wet aluminium surface by the steps of:

- (a) cleaning the surface of the aluminium article, already pre-formed to the shape and size intended for final use, by contacting it for an effective time with an aqueous-based liquid cleaning composition so constituted as to produce a thoroughly-degreased, clean surface substantially free from aluminium fines and other solid contamination; and
- (b) rinsing the thus-cleaned surface with additional water.

The process of the invention also, almost inevitably, will normally include the subsequent step of drying the treated surface.

The process of the invention is best applied to formed aluminium articles, which will desirably be treated by contacting them with the multi-component composition at an effective temperature for such a period as to ensure that after drying the treated surface has a coefficient of static surface friction of less than 1.5. Aluminium

articles such as cans after they have been treated and dried can then very readily be conveyed, with increased mobility, via high-speed automatic conveying equipment to a lacquering and/or printing station.

It has been found desirable in the process according to the invention to employ as component (A) a compound of general formula I wherein each of R^1 , R^3 and R^6 is hydrogen, each of x and z is zero, and y is not less than about 0.5 times the number of carbon atoms in R^4 .

It has also been found preferable to employ a liquid composition in which:

- (i) the concentration of phosphorus is in the range from about 0.00001 to about 0.0032 gram atoms per litre;
- (ii) the total concentration of all the metal atoms in component (B) is in the range from about 0.00001 to about 0.01 gram atoms per litre;
- (iii) the total concentration of components (A), (B) and (C) is between about 0.005 and about 0.05 % by weight;
- (iv) the pH is between 2 and about 5; and
- (v) the temperature during contact with the aluminium surface is between 21° and 54°C .

Furthermore it is advantageous if the ratio by weight of component (D) to component (E) is in the range of from 3:1 to 1:3, and the ratio by weight of the combined components (D) and (E) to component (A) is in the range of

the formed aluminium surface is preferably from 10 to 85°C, more desirably from 21 to 54°C.

Contact may be effected by spraying, immersion or any other convenient method, or combination of methods. Preferably the time of contact is from 5 to 60 seconds more preferably 20 to 30 seconds.

It is also generally preferable to rinse the treated surface first with tap water and then again with deionized water after treatment according to the invention and before further processing, such as drying, printing, lacquering or the like.

In yet another of its aspects, this invention also provide concentrates from which the composition to be used for treating can be made by dilution with water. Such a concentrate preferably contains the components (A), (B), (C), and optionally (D), (E), (F) and/or (G) as noted above, in concentrations some 30 to 200 times greater than those employed, as noted above, in the ready-for-use compositions.

The processes and compositions used in accordance with this invention display clear advantages over anything herebefore available, for instance:

- after treatment according to this invention, a surface can be rinsed with tap or deionized water, without losing its improved surface mobility and other advantages, many more times than a surface treated according to the Examples of

the aforesaid United States Patent No. 4,859,351;

- if there is prolonged contact between the treated surface and a cleaning composition or one of the rinses after cleaning but prior to treatment with a composition according to this invention (for example as a result of unplanned stoppages of a high-speed production line), light-to-deep brown spots, believed to be hydrated aluminium oxide, sometimes form on the treated surface; any such spots are removed by treatment according to this invention, whereas they usually persist after using a process as taught in the Examples of the aforesaid United States Patent No. 4,859,351;

- a process according to this invention may more readily be operated at a pH sufficiently low to inhibit bacterial growth than one according to the Examples of the aforesaid United States Patent No. 4,859,351;

- almost any readily-available industrial or tap water supply may be used for make-up or dilution of a composition according to this invention, while the compositions disclosed in the aforesaid United States Patent No. 4,859,351 generally needs deionized water for best results; and

- the surfaces produced by a process according to the present invention are very readily wetted by water and thus remain free from "water breaks", which are considered

undesirable by most aluminium can processors, whereas cans processed according to the Examples of the aforesaid Unit d States Patent No. 4,859,351 are much more likely to exhibit water breaks.

As just indicated above, it is one of the advantages of the multi-component compositions herein disclosed that they may be used in the processes at a pH so acidic that bacterial growth is inhibited, and resultant degradation thereby avoided. However, the multi-component compositions may be operated successfully over quite a wide range of pH values, not all of which will necessarily be inhibitory. It is therefore a further preferred feature of this invention that in order to extend their resistance to biodegradation the compositions, as employed in the process, should also include an effective amount of a biocide. It has moreover been found that as biocide it is most advantageous to employ hydrogen peroxide.

In the application of the compositions to bring them into contact with the aluminium or other metallic surface there can be problems created by foaming, and it is therefore another preferred feature of this invention that the composition should also include an effective amount of an anti-foaming agent.

It is indeed a specific, much preferred further feature of this invention to provide in processes for conditioning

pre-cleaned metallic surfaces to increase their mobility the step of protecting the mobility-enhanced compositions employed thereon against deterioration by micro-organisms during storage and use, and/or protecting them from foaming during preparation and use, by incorporating in said compositions an effective amount of one or more biocides, and/or an effective amount of one or more anti-foam agents.

Specifically, this invention provides a process comprising the steps of cleaning an aluminium can with an aqueous acidic or alkaline cleaning solution, drying the cleaned can, and subsequently conveying the cleaned and dried can via automatic conveying equipment to a location where it is lacquered and/or decorated by printing, wherein the improvement comprises contacting at least one surface of said aluminium can, prior to the last drying of said exterior surface before automatic conveying, with a mobility-enhancing lubricant and surface-conditioner composition containing:

- a biocidal material in an amount effective to prevent deterioration of the lubricant and surface-conditioner composition during storage or use; and/or
- an anti-foam agent in sufficient amount to significantly reduce foaming during the process;

so as thus to form a film on the can surface and thereby to import to the surface of the can after drying a reduced

coefficient of static friction that is not more than 1.5.

The lubricant and surface-conditioner composition may be an aqueous solution consisting essentially of an aqueous solution of hydrogen peroxide, and one or more of the following organic materials, namely ethoxylated phosphate esters, ethoxylated alcohols, ethoxylated fatty acids, ethoxylated hydroxy-substituted fatty acids and salts, amides, ethers and esters of ethoxylated fatty acids, and of ethoxylated hydroxy-substituted fatty acids.

The lubricant and surface-conditioner composition normally has a pH between about 1 and 6.6, preferably between 2.5 and 5. The dissolved organic material may advantageously be any one or more of the following ethoxylates, namely ethoxylated fatty acids, salts of ethoxylated fatty acids, ethoxylated alcohols having at least 4 carbon atoms and containing up to about 20 moles of condensed ethylene oxide per mole of alcohol, and ethoxylated alkyl alcohol phosphate esters.

Any antimicrobial or biocidal agent, except those having some detrimental effect on the mobility-enhancing properties or the stability of the compositions as previously taught herein in an amount sufficient to effectively inhibit the growth of microorganisms. Hydrogen peroxide is generally most preferred for this purpose. In aqueous concentrated compositions, suitable for dilution

with about 99 times their own weight of water to make a composition ready for direct application to metal to enhance mobility after drying, as already described, concentrations of hydrogen peroxide in the range from 0.375 to 3.75 % are preferred, with concentrations in the range from 1.4 - 2.2% most preferred. In more concentrated compositions the preferred biocide concentrations would be determined by the expected degree of dilution of the concentrate. In general, however, because of the relatively low stability of concentrated hydrogen peroxide, it is preferred that this component, if used, be added only to a sufficiently dilute concentrate that the concentration of hydrogen peroxide does not exceed about 3 wt%. at the time of making up the composition.

Any antifoam agent, except those which have some detrimental effect on the mobility-enhancing properties already described or the stability of the compositions, may advantageously be added to the compositions as previously taught herein, in an amount effective to decrease the amount of foaming observed during preparation and/or use of the compositions. The preferred antifoam agent is a combination of wax, low volatility liquid paraffin hydrocarbons, and high molecular weight fatty acid derivatives. Generally, silicone antifoam agents are not desirable for use with this invention because they tend to

cause formation of water breaks. An amount of antifoam agent corresponding to 0.05 to 2 wt% is generally preferred, with 0.5 to 1 wt% usually more preferred.

All the advantages of increased mobility, low surface coefficient of friction, high quality printability, and good adhesion of lacquers and the like as taught in the aforesaid United States Patent No. 4,589,351 are retained for treatments according to this invention.

In order that the invention may be well understood it will now be described in more detail, though only by way of illustration, with reference to the following working examples and comparative examples:

EXAMPLES

General conditions for Examples 1 - 7 and Comparison

In all these examples, the surfaces treated were those of conventional aluminium beverage cans already in their final shape and size. The cans were subjected to an acid prewash in an aqueous sulfuric acid having a pH of 2 for 30 seconds ("sec") at 54°C, then to washing with a conventional alkaline, surfactant-containing cleaner at pH 12.3 for 60 sec at 54°C, and then to a 30 sec tap water rinse before being treated with a composition according to this invention as set forth in the specific examples below. (The compositions given in the specific examples are for concentrates according to this invention; for treatment, a

solution of the w% of the concentrate specified in Table 1, in tap water, was used.) After this treatment, the cans were rinsed first in tap water for 30 sec, then in deionized water for 90 sec, and dried at 210°C.

The cans were evaluated for their coefficient of static friction using a laboratory static friction tester. This device measures the static friction of associated with the surface characteristics of aluminium cans. This is done by using a ramp which is raised through an arc of 90° by using a constant speed motor, a spool and a cable attached to the free swinging end of the ramp. A cradle attached to the bottom of the ramp is used to hold 2 cans in horizontal position approximately 0.5 inches apart with the domes facing the fixed end of the ramp. A third can is laid upon the 2 cans with the dome facing the free swinging end of the ramp, and the edges of all 3 cans are aligned so that they are even with each other.

As the ramp begins to move through its arc a timer is automatically actuated. When the ramp reaches the angle at which the third can slides freely from the 2 lower cans, a photoelectric switch shuts off the timer. It is this time, recorded in seconds, which is commonly referred to as "slip time". The coefficient of static friction is equal to the tangent of the angle swept by the ramp at the time the can begins to move.

Example 1

A concentrate was prepared with the following composition:

| <u>Ingredient</u> | <u>Parts by Weight in Composition</u> |
|------------------------------|---------------------------------------|
| Stannic chloride solution | |
| 25% by weight in water | 300 |
| ETHFAC TM 136 | 400 |
| ETHOX TM MI-14 | 100 |
| Ammonium bifluoride solution | |
| 25% by weight in water | 135 |
| DEQUEST TM 2010 | 25 |
| Water | 9040 |
| | ----- |
| | 10,000 |
| | ----- |

ETHFACTM 136, commercially-available from Ethox Chemicals, Inc., of Greenville, South Carolina, U.S.A. is an ethoxylated alkyl alcohol phosphate ester.

ETHOXTM MI-14, commercially-available from Ethox Chemicals, Inc., of Greenville, South Carolina, U.S.A. is an ethoxylated non-ionic surfactant.

Example 2

A concentrate was prepared with the following composition:

| <u>Ingredient</u> | <u>Parts by Weight in Composition</u> |
|---|---|
| Ferric ammonium citrate solution, 25% by weight in water | 300 |
| ETHFAC TM 136 | 400 |
| ETHOX TM MI-14 | 100 |
| Ammonium bifluoride solution, 25% by weight in water | 135 |
| DEQUEST TM 2010 | 25 |
| Water | 9040 |
| | ----- |
| | 10,000 |
| | ----- |

Example 3

A concentrate was prepared with the following composition:

| <u>Ingredient</u> | <u>Parts by Weight in Composition</u> |
|---|---|
| Cerium ammonium sulfate | 4 |
| ETHFAC TM 136 | 30 |
| Ammonium bifluoride solution, 25% by weight in water | 16 |
| DEQUEST TM 2010 | 2 |
| Sulfuric acid | 1 |
| TRITON TM 101 | 5 |
| Water | 942 |
| | ----- |
| | 1,000 |

Example 4

A concentrate was prepared with the following composition:

| <u>Ingredient</u> | <u>Parts by Weight in Composition</u> |
|---|---------------------------------------|
| Aluminium chloride | 10 |
| ETHFAC TM 136 | 50 |
| Ammonium bifluoride solution, 25% by weight in water | 11 |
| TRITON TM N101 | 6 |
| Citric acid | 6 |
| Ethoxylated alcohol surfactant | 11 |
| Water | 906 |
| | ----- |
| | 1,000 |

Example 5

A concentrate was prepared with the following composition:

| <u>Ingredient</u> | <u>Parts by Weight in Composition</u> |
|---|---------------------------------------|
| Fluorozirconic acid | 15 |
| Mono(hexyltriethoxy) phosphate | 70 |
| Poly (oxyethylene) isostearate with an average of 14 oxyethylene units per isostearate unit | 20 |
| Ammonium bifluoride solution 25% by weight in water | 19 |
| Aminoacetic acid | 20 |
| Water | 856 |
| | ----- |
| | 1,000 |

Example 6

A concentrate was prepared with the following composition:

| <u>Ingredient</u> | <u>Parts by Weight in Composition</u> |
|---|---------------------------------------|
| Fluorozirconic acid | 15 |
| Mono(hexyltriethoxy) phosphate | 30 |
| ETHOX TM MI-14 | 20 |
| Ammonium bifluoride solution, 25% by weight in water | 15 |
| Butane-2-phosphonic acid tricarboxylate | 10 |
| Water | 910 |
| | ----- |
| | 1,000 |

Example 7

A concentrate was prepared with the following composition:

| <u>Ingredient</u> | <u>Parts by Weight in Composition</u> |
|---|---------------------------------------|
| Fluorozirconic acid | 10 |
| Polyoxyethylene isostearate containing an average of 14 moles of -C ₂ H ₄ O- groups per mole of isostearate | 10 |
| TRITON TM H-66 | 80 |
| DEQUEST TM 2010 | 2.5 |
| Ammonium bifluoride solution, 25% by weight in water | 4 |
| Water | 893.5 |
| | ----- |
| | 1,000 |

In the composition given above, DEQUEST 2010 is a trade name for a material that is reported to be predominantly 1-hydroxyethylidene-1-diphosphonic acid, and TRITON N101 is a trade name for a surfactant material that is reported to be predominantly nonylphenoxyxypoly(ethoxy)ethanol, with an average of 9 - 10 ethoxy groups per molecule.

Table 1 shows the specific amounts of the concentrates used, treatment conditions, and the coefficients of static surface friction achieved on the cans by sorption of a lubricant and surface-conditioning layer for these examples.

Table 1
IMPROVEMENT IN SURFACE FRICTION FROM TREATMENT ACCORDING TO
THIS INVENTION

| Experiment Number | % by Weight of Concentrate in Treatment | Treatment Temperature Degrees C | Conditions Time Seconds | Coefficient of static Surface friction |
|-------------------|---|---------------------------------|-------------------------|--|
| 1 | 1.0 | 35 | 20 | 1.27 |
| 2 | 1.0 | 35 | 20 | 1.47 |
| 3 | 1.0 | 35 | 20 | 1.31 |
| 4 | 1.0 | 35 | 20 | 0.77 |
| 5 | 1.0 | 35 | 20 | 0.77 |
| 6 | 1.0 | 35 | 20 | 1.20 |
| 7 | 1.0 | 35 | 20 | 1.01 |
| No treatment | | | | 1.67 |

Example 8

This is an example of a composition that contains a preferred antifoam agent and a preferred biocide, but otherwise is according to the teachings of the aforesaid United States Patent No. 4,859,351.

A first concentrate is prepared by mixing 880 parts by weight of ETHOXTM MI-14, 60 parts by weight of COLLOID 999TM (a high molecular weight fatty acid derivative, available commercially from Colloids, Inc., 394 Frelinghuysen Ave., Newark, New Jersey 07114, U.S.A.) and 60 parts by weight of GP-295TM Defoamer (a suspension of about 10% solid wax in white mineral oil, available commercially from Genese Polymers Corp., Flint, Michigan 48507, U.S.A.). The ETHOXTM MI-14 is first melted in a mixing tank at 27 - 32°C. The other two materials are then added in the order noted, and mixed to form a cloudy but visually-homogenous liquid with no lumps.

A second concentrate suitable for storage for at least several months is then made by mixing 47 parts by weight of the first concentrate described above with 917 parts by weight of water, preferably deionized water, and with 40 parts by weight of 37.5% aqueous hydrogen peroxide. This

second concentrate may then be diluted when desired to make a composition suitable for directly treating aluminium surfaces, in the manner already generally described in United States Patent No. 4,859,351.

Examples 9 and 10

These examples illustrate preferred stabilized compositions including metal-containing salts and ethoxylated phosphates. The compositions set forth in Table 2 below are concentrates, suitable for use in treating metal containers after being diluted with e.g. 50 - 200 times their own weight of tap water.

Table 2: COMPOSITIONS FOR EXAMPLES 9 AND 10

| Ingredient | Parts by weight in Example No.: | |
|--|------------------------------------|-----|
| | 9 | 10 |
| Deionized water | 920 | 856 |
| ETHOX TM 2684 | 14 | 60 |
| TRITON TM DF-16 | 12 | - |
| TRYCOL TM LF-1 | 4 | 30 |
| IGEPAL TM CO-880 | 11 | 30 |
| DEQUEST TM 2010 | 3 | 1 |
| Ammonium bifluoride NH ₄ F.HF) | 11 | 4 |
| Fluorozirconic acid (H ₂ ZrF ₆) | 25 | 20 |

Sources and characteristics of ingredients in Table 2 not previously identified are as follows:

ETHOXTM 2684, commercially-available from Ethox Chemicals, Inc., Greenville, South Carolina 20606, USA, corresponds to general formula I where x and z are both zero, R², R³ and R⁵ all represent hydrogen, R⁴ represents a mixture of C₈₋₁₀ linear alkyl groups, and y averages about 15.

TRITONTM DF-16, commercially-available from Rohm & Haas, Philadelphia, Pennsylvania 19105, U.S.A., is reported to be a modified polyethoxylated straight chain alcohol.

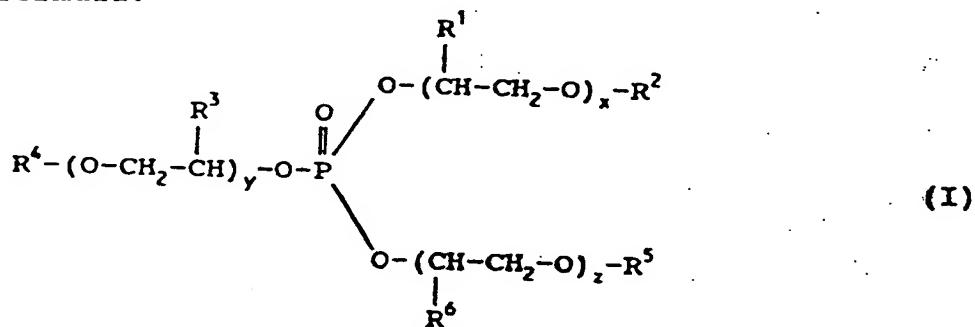
TRYCOLTM LF-1, commercially-available from the Emery Chemical Division of Penkel Corporation, Cincinnati, Ohio 45249, USA, is reported to be an alkyl polyether.

IGEPALTM CO-880, commercially-available from GAF Corp, Wayne, New Jersey 07470, USA, is reported to be an ethoxylated nonyl phenol.

CLAIMS

1. A process in which the surface of a previously-formed aluminium article, already degreased and cleaned to remove aluminium fines and other solid contamination therefrom and thereafter water-rinsed, is treated while still wet from the water-rinse by contact with a liquid, aqueous multi-component composition which besides water comprises:

-(A) one or more water-soluble materials conforming to the general formula:



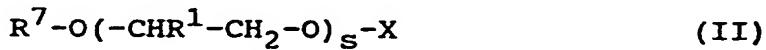
(wherein each of R^1 , R^3 and R^6 , which may be the same or different, is hydrogen or an alkyl group containing from 1 to 4 carbon atoms, each of x , y and z is zero or an integer from 1 to 25, and each of R^2 , R^4 and R^5 , which may be the same or different, is hydrogen or a monovalent cation or a monovalent fraction of a polyvalent cation or an alkyl, aryl or arylalkyl group containing from 1 to 20 carbon atoms,

provided however that at least one of R^2 , R^4 and R^5 (i) is not hydrogen and (ii) has at least one alkoxy group interposed between it and the phosphorous atom;

-(B) one or more water-soluble salts containing ions that include one or more Fe, Zr, Sn, Al and/or Ce atom(s);

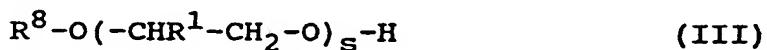
-(C) one or more water-soluble metal-etching compounds;

-(D) one or more compounds conforming to the general formula:



(wherein R^7 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 1 to 25 carbon atoms, X is hydrogen, halogen, phenyl or R^1 , while S is an integer from 1 to 50, and R^1 has the same meaning as in general formula I); and

-(E) one or more compounds conforming to the general formula:



(wherein R^8 is a linear, cyclic, or branched saturated monovalent aliphatic hydrocarbon moiety containing from 4 to 25 carbon atoms, (C_6H_4) is an ortho-, meta-, or para-phenylene nucleus, and R^1 and S have the same meanings as in general formula II above),

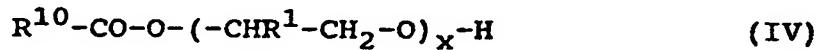
the amounts of components of (D) and (E) being sufficient to stabilize the liquid composition against phase-separation.

2. A process as claimed in claim 1, in which said multi-component composition also comprises:

-(F) one or more chelating agents for the metal-containing ions of component (B).

3. A process as claimed in claim 1 or claim 2, in which said multi-component composition also comprises:

-(G) one or more compounds conforming to the general formula:



(wherein R^{10} is a linear or branched, saturated or unsaturated monovalent aliphatic hydrocarbon moiety containing from 1 to 25 carbon atoms; and R^1 and x have the same meaning as in general formula 1).

4. A process as claimed in any of the preceding claims, which includes the preliminary preparation of the degreased cleaned and still-wet aluminium surface by the steps of:

(a) cleaning the surface of the aluminium article, already pre-formed to the shape and size intended for final use, by contacting it for an effective time with an aqueous-based liquid cleaning composition so constituted as to produce a

thoroughly-degreased, clean surface substantially free from aluminium fines and other solid contamination; and

(b) rinsing said cleaned surface with additional water.

5. A process as claimed in any of the preceding claims, which includes the subsequent step of drying the treated surface.

6. A process as claimed in claim 5, in which aluminium articles are treated by contacting them with the multi-component-composition at an effective temperature for such a period as to ensure that after drying the treated surface its coefficient of static surface friction is less than 1.5.

7. A process as claimed in claim 6, in which the treated and dried aluminium articles are thereafter conveyed via high-speed automatic conveying equipment to a lacquering and/or printing station.

8. A process as claimed in any of the preceding claims, in which component (A) is a compound of general formula I wherein each of R^1 , R^2 and R^6 is hydrogen, each of x and z is zero, and y is not less than 0.5 times the number of carbon atoms in R^4 .

9. A process as claimed in any of the preceding claims, in which in said liquid composition

- (i) the concentration of phosphorus is in the range of from 0.00001 to 0.0032 gram atoms per litre;
- (ii) the total concentration of all the metal atoms in component (B) is in the range of from 0.00001 to 0.01 gram atoms per litre;
- (iii) the total concentration of components (A), (B) and (C) is between about 0.005 and about 0.05 percent by weight;
- (iv) the pH is between 2 and 5; and
- (v) the temperature during contact with the aluminium surface is between 21° and about 54°C.

10. A process as claimed in any of the preceding claims, in which the ratio by weight of component (D) to component (E) is in the range of from 3:1 to 1:3, and the ratio by weight of the combined components (D) and (E) to component (A) is in the range of from 3.3:1 to 1:2.

11. A process as claimed in claim 10, in which the ratio by weight of component (D) to component (E) is in the range of from 1.7:1 to 1:1.4, and the ratio by weight of the combined components (D) and (E) to component (A) is in the range of from 1.8:1 to 1:1.5.

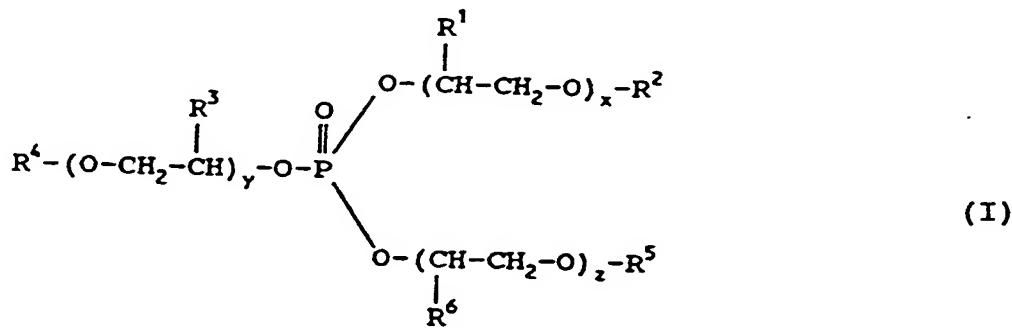
12. A process as claimed in any of the preceding claims, in which component (D) is a compound conforming to general

formula II wherein R¹ is hydrogen, R⁷ contains 4 - 20 carbon atoms, and s is an integer from 1 to 20; and component (E) is a compound conforming to general formula III wherein R¹ is hydrogen, R⁸ contains 8 - 12 carbon atoms, and s is an integer from 1 to 20.

13. A process as claimed in any of the preceding claims and substantially as herein described.

14. A liquid, aqueous multi-component composition, for use in the process claimed in any of the preceding claims, which besides water comprises:

-(A) one or more water-soluble materials conforming to the general formula:



(wherein each of R¹, R³ and R⁶, which may be the same or different, is hydrogen or an alkyl group containing from 1 to 4 carbon atoms, each of x, y and z is zero or an integer from 1 to 25, and each of R², R⁴ and R⁵, which may be the

same or different, is hydrogen or a monovalent cation or a monovalent fraction of a polyvalent cation or an alkyl, aryl or arylalkyl group containing from 1 to 20 carbon atoms, provided however that at least one of R^2 , R^4 and R^5 (i) is not hydrogen and (ii) has at least one alkoxy group interposed between it and the phosphorous atom;

-(B) one or more water-soluble salts containing ions that include one or more Fe, Zr, Sn, Al and/or Ce atom(s);

-(C) one or more water-soluble metal-etching compounds;

-(D) one or more compounds conforming to the general formula:



(wherein R^7 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 1 to 25 carbon atoms, X is hydrogen, halogen, phenyl or R^1 , while s is an integer from 1 to 50, and R^1 has the same meaning as in general formula I); and

-(E) one or more compounds conforming to the general formula:



(wherein R^8 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 4 to

25 carbon atoms, (C_6H_4) is an ortho-, meta-, or para-phenylene nucleus, and R^1 and s have the same meanings as in general formula II above),

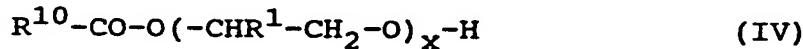
the amounts of components (D) and (E) being sufficient to stabilize the liquid composition against phase-separation.

15. A composition as claimed in claim 14, which also comprises:

-(F) one or more chelating agents for the metal-containing ions of component (B).

16. A composition as claimed in claim 14 or 15, which also comprises:

-(G) one or more compounds conforming to the general formula:



(wherein R^{10} is a linear or branched, saturated or unsaturated monovalent aliphatic hydrocarbon moiety containing from to 25 carbon atoms; and R^1 and x have the same meaning as in general formula 1).

17. A composition as claimed in any of claims 14 to 16, in which component (A) is a compound of general formula I wherein each of R^1 , R^2 and R^6 is hydrogen, each of x and z is zero, and y is not less than 0.5 times the number of

carbon atoms in R^4 .

18. A composition as claimed in any of claims 14 to 17, in which:

- (i) the concentration of phosphorus is in the range from 0.00001 to 0.0032 gram atoms per litre;
- (ii) the total concentration of all the metal atoms in component (B) is in the range from 0.00001 to 0.01 gram atoms per litre;
- (iii) the total concentration of components (A), (B) and (C) is between 0.005 and 0.05 percent by weight; and
- (iv) the pH is between 2 and 5.

19. A composition as claimed in any of claims 14 to 18, in which the ratio by weight of component (D) to component (E) is in the range of from 3:1 to 1:3, and the ratio by weight of the combined components (D) and (E) to component (A) is in the range of from 3.3:1 to 1:2.

20. A composition as claimed in any of claims 14 to 19, in which the ratio by weight of component (D) to component (E) is in the range of from 1.7:1 to 1:1.4, and the ratio by weight of the combined components (D) and (E) to component (A) is in the range of from 1.8:1 to 1:1.5.

21. A composition as claimed in any of claims 14 to 29, in

which component (D) is a compound conforming to general formula II wherein R¹ is hydrogen, R⁷ contains 4 - 20 carbon atoms, and s is an integer from 1 to 20; and component (E) is a compound conforming to general formula III wherein R¹ is hydrogen, R⁸ contains 8 - 12 carbon atoms, and s is an integer from 1 to 20.

22. A liquid aqueous multi-component composition as claimed in any of claims 14 to 21, and substantially as herein described.

23. A composition as claimed in any of claims 14 to 22, which also includes an effective amount of a biocide.

24. A composition as claimed in any of claims 14 to 23, which also includes an effective amount of an anti-foaming agent.

25. Processes for conditioning the pre-cleaned surfaces of pre-formed metallic articles to increase their mobility in subsequent automatic handling operations by treatment thereof with an aqueous lubricant and surface-conditioning composition based on water-soluble ethoxylated organic materials, wherein the mobility-enhancing compositions employed are protected against impairment by incorporating therein an effective amount of one or more biocide(s) and/or

one or more anti-foaming agents.

26. A process as claimed in claim 25, comprising the steps of cleaning an aluminium can with an aqueous acidic or alkaline cleaning solution, drying the cleaned can, and subsequently conveying the cleaned and dried can via automatic conveying equipment to a location where it is lacquered and/or decorated by printing, wherein the improvement comprises contacting at least one surface of said aluminium can, prior to the last drying of said exterior surface before automatic conveying, with a mobility-enhancing lubricant and surface-conditioner composition containing:

- a biocidal material in an amount effective to prevent deterioration of the lubricant and surface-conditioner composition during storage or use; and/or

- an anti-foam agent in sufficient amount to significantly reduce foaming during the process;

so as thus to form a film on the can surface and thereby to impart to the surface of the can after drying a reduced coefficient of static friction that is not more than 1.5.

27. A lubricant and surface-conditioner composition for use in the process claimed in claim 25 or claim 26, in which the

ethoxylated organic material(s) employed is/are one or more of the following, namely ethoxylated phosphate esters, ethoxylated alcohols, ethoxylated fatty acids and ethoxylated hydroxy-substituted fatty acids, as well as salts, amides, ethers and esters of ethoxylated fatty acids and of ethoxylated hydroxy-substituted fatty acids which composition has a pH between about 1 and 6.6, and which also incorporates an effective amount of one or more biocides and/or one or more anti-foaming agents.

28. A composition as claimed in claim 27, which has a pH in the range of from 2.5 to 5.

29. A composition as claimed in claim 27 or claim 28, in which the organic material(s) employed is/are ethoxylated fatty acids, salts of ethoxylated fatty acids and ethoxylated alcohols having at least 4 carbon atoms and containing up to about 20 moles of condensed ethylene oxide per mole of alcohol, and ethoxylated alkyl alcohol phosphate esters.

30. A composition as claimed in any of claims 27 to 29, in which the biocide is or includes hydrogen peroxide.

31. Aqueous concentrated compositions as claimed in claim 30, suitable for dilution with about 99 times their own

weight of water to make a composition ready for direct application to metal to enhance mobility after drying, in which the concentration of hydrogen peroxide is in the range from 0.375 to 3.75 %.

32. Concentrates as claimed in claim 31, wherein hydrogen peroxide is present in a concentration in the range from 1.4 - 2.2%.

33. A composition as claimed in any of claims 27 to 31, in which the antifoaming agent is or includes a combination of wax, low-volatility liquid paraffin hydrocarbons, and high molecular weight fatty acid derivatives.

34. A composition as claimed in claim 32, in which the anti-foaming agent is present in a concentration of from 0.05 to 2% by weight.

35. A composition as claimed in claim 33, in which the anti-foaming agent is present in a concentration of from 0.5 to 1% by weight.